Determination of Ultra Low Contents of Oxygen in High Purity Iron[†]

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Determination of trace oxygen in high purity iron was studied using a LECO TC-436 oxygen/nitrogen determinator. Examined were oxygen blanks due to helium carrier gas, apparatus and graphite crucibles. The blank due to helium carrier gas was reduced and stabilized by using a gas refining system usable for twelve months or more without repack of reagents. The blank in the apparatus was reduced and stabilized by removing the water adsorbed on the wall of a carrier gas tube. The blank in a double graphite crucible was significantly lowered by using an outer crucible deoxidized with silicon at 2373 K and an inner one degassed at 2573 K for 120 s. As a result of these improvements, the blank value for oxygen analysis using the LECO determinator decreased to less than 0.01 mass ppm O. Moreover, four kinds of pretreatments of an analytical specimen were examined, and hydrogen reduction following electro-polishing was found to be particularly effective. Gas extraction from the pretreated specimen was carried out with a power of 3.1 ± 0.2 kW (2373 K) for 100 s. As a bath material, 0.75 g of Sn was used for 1 g of the sample. The proposed procedure was successfully applied to the analysis of two kinds of high purity iron samples with different oxygen contents. The RSD-values were 8.3% for 1.2 mass ppm O and 1.1% for 4.8 mass ppm O. The analytical values thus determined were in good agreement with those by charged particle activation analysis.

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I. Introduction

With a significant advance in the preparation of high purity iron⁽¹⁾, analytical techniques for trace oxygen are being interested. Chemical Characterization Sub-committee of the 19th Committee (steel making) in the Japan Society for the Promotion of Science (JSPS) conducted a cooperative research on the determination of trace oxygen in high purity iron⁽²⁾⁽³⁾. This paper describes the experiments carried out in our Institute in relation to the JSPS cooperative research. In the current analysis of oxygen in steel and iron materials, inert gas fusion method using impulse heating is widely used. In recent years, highly sensitive apparatus for the method have been commercially available. However, the limits of determination given by these apparatus are too high for the determination of ppm-level oxygen, because of blanks. Moreover, there are difficulties to apply the conventional analytical procedure used in the oxygen determination to the determination of trace oxygen in high purity iron. Special attention should be paid to lower oxygen blanks.

In general, the blanks of the oxygen analysis by the inert gas fusion method arise in each of carrier gas, graphite crucible and apparatus itself. However, the previous papers⁽⁴⁾⁻⁽⁶⁾ have not referred to the blank sources except the graphite crucible used. In this study, all of those three sources were examined. Moreover, optimum operating conditions of the apparatus and procedures for pretreating an analytical specimen were

examined, and a rapid and accurate procedure was established for the determination of trace oxygen in high purity iron.

II. Experimental Procedure

1. Analytical apparatus

A LECO TC-436 type oxygen and nitrogen determinator (LECO, USA) was used. Main performance and characteristics of the determinator are as follows:

- (1) Analytical range: 0.1 ppm–0.1% at 1 g of sample
- (2) Analytical sensitivity: 0.1 ppm
- (3) Minimum unit of indicator: 0.01 ppm
- (4) Detection method: Infrared absorption after CO/CO₂ conversion
- (5) Gas extraction: Inert gas fusion by impulse heating
- (6) Carrier gas: Helium of 99.995% pure
- (7) Gas flow rate: Carrier gas: 450 cm³/60 s,
Reference gas: 30 cm³/60 s

A double graphite crucible was used to melt an analytical specimen. The crucible was composed of an inner graphite crucible (LECO 775-431, 10.8 mm in I.D. and 14.4 mm deep) and an outer one (LECO 775-433, 12.9 mm in I.D. and 20.3 mm deep). A two-color radiation thermometer was used to measure the temperature of an impulse-heated graphite crucible.

The maximum temperature attainable for the double graphite crucible was in the range of about 2573 to 2673 K; therefore, a degassing power of 4.5 ± 0.2 kW (about 2573 K) and an extraction power of 3.1 ± 0.2 kW (about 2373 K) were selected.

In order to purify the helium carrier gas, a gas refining

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Fig. 1 Gas flow diagram of the TC-436 oxygen and nitrogen determinator. IR: Infrared rays detector, TCD: Thermal conductivity detector.

system with a large capacity was attached to the oxygen/nitrogen determinator. The system consisted of a "Dry Column" (Nikka Seiko, Japan) packed with 0.5 kg of a dehydrating agent and a "Gas Clean" column (Nikka Seiko) packed with 0.5 kg of a deoxidizing agent. The former is capable of lowering a dew point of the applied gas to below 193 K and the latter has an oxygen absorption capacity of 160 cm³ at NTP. Figure 1 shows the gas flow diagram of the LECO oxygen/nitrogen determinator equipped with the gas refining system.

2. Analytical samples

Two kinds of high purity irons⁽¹⁾ with different oxygen contents were analyzed. The iron samples (5 mm in diameter and 150 mm long) were provided from the Institute for Materials Research of Tohoku University. Short pieces were cut from each sample rod with a high speed cutter having a thin blade, and they were used as analytical specimens after degreasing in petroleum benzene. The weight of a specimen was adjusted to about 1 g by considering sufficient melting and complete gas extraction, although a specimen as large as possible was acceptable from the viewpoint of the amount of oxygen to be analyzed.

3. Pretreatment of high purity iron sample

In general, an analytical specimen suffers surface contamination in the course of its preparation, owing to surface oxidation, adhesion of abrasives and adsorption of water molecules. For the correct determination of trace oxygen in the bulk of the sample, surface contaminants should be entirely removed. Hence, the several kinds of pretreatments were examined for the analytical specimen of high purity iron. Each specimen was analyzed without delay after the pretreatment.

Method (a) Chemical polishing was carried out using a solution: HF(46.5%), 30 cm³; H₂O₂(30%), 500 g; and H₂O⁽⁷⁾, 60 cm³. The solution was cooled below 273 K, in which a specimen was soaked for 60 s. After the specimen had been treated with a stopping solution (a mixture of 100 cm³ each of H₂O₂ and H₂O), the specimen was rinsed in turn with distilled water, ethanol and acetone, and dried in a hot stream of air⁽⁸⁾.

Method (b) Electro-polishing was carried out in a

mixed solution of 10 v/v% CH₃COOH and 1 v/v% HClO₄⁽⁹⁾. The cathode was a stainless steel vessel and the anode was a mild steel rod, to which the specimen was electromagnetically attached. A direct current of 10 V and 1 A was applied. Since the electrolysis accompanied the generation of heat, the electro-polishing solution was cooled to below 293 K. After 360 s electrolysis, the specimen was turned upside down and electrolyzed again for more 120 s. The specimen was then rinsed and dried in the same manner as described in (a).

Method (c) Electro-polishing was carried out in a methanol solution containing 10 v/v% acetyl acetone and 1 v/v% tetramethylammonium chloride⁽²⁾⁽¹⁰⁾. The procedure of electrolysis was the same as that described in (b). However, electrolysis time was changed to 180 s each for one face and for the other face of the specimen, taking account of the strong polishing action of this solution.

Method (d) An apparatus as shown in Fig.2 was used for surface treatment. A separable sample container which could carry a sample without exposure to the air was attached to the apparatus. A specimen which had been polished by method (c) was placed in the furnace of the apparatus. The specimen was heated to 673 K in an Ar-5% H₂ flow of 500 cm³/60 s and its surface was reduced for 600 s⁽⁶⁾. The specimen was then cooled in the gas stream and dropped into the sample container filled with helium. The container was carried to the impulse furnace and the specimen was admitted to the analysis. In Fig. 2, the portion to be heated was made from quartz and the other portion from Pyrex glass. The transfer of the specimen was carried out with a sample transferring tube through two O-ring seals.

4. Calibration curve

A calibration curve was prepared by using JSS-GS-6a

Fig. 2 The apparatus for elimination of surface oxygen on specimens.

(O: 3.4 mass ppm), JSS-GS-2b (O: 14.6 mass ppm) and JSS-GS-3b (O: 38.5 mass ppm) as reference materials. Before use, GS-6a (granular sample immersed in oil) was rinsed in difron and ether three times by using ultra sonic wave. While, GS-2b and GS-3b (pin samples packed with stain-proof papers) were electrolytically polished⁽⁹⁾. The calibration curve was prepared for every series of experimental runs.

5. Proposed procedure for determination

The procedure proposed in this study for the determination of trace oxygen in high purity iron is as follows.

(1) Pass a current of helium through the carrier gas tube reaching the TC-436 apparatus at a rate of 450 cm³/60 s. Hold the temperature of the gas tube (about 2 m) at 403 K for more than 7.2 ks by using tape heaters.

(2) Add 25 mg of Si chips in an outer crucible and heat the crucible for 80 s with a power of 4.5 ± 0.2 kW (about 2573 K). Outgas the crucible for 100 s with a power of 3.1 ± 0.2 kW (about 2373 K), and confirm that the oxygen blank value indicated for 1 g of the sample is below 0.01 mass ppm O/100 s.

(3) Place an inner crucible in the outer crucible deoxidized with Si and outgas the inner crucible by heating with the outer one for 60 s with a power of 4.5 ± 0.2 kW.

(4) Open the impulse furnace and add 0.75 g of Sn chips into the double crucible. Close the furnace and outgas the molten Sn for 60 s with the same power as that in (3).

(5) After weighing 1 g of sample, charge it into the double crucible and carry out gas extraction with a power of 3.1 ± 0.2 kW until the amount of the evolved gas becomes undetectable (about 90 s).

In the procedure mentioned above, the outer crucible can withstand its repeated use of 3 to 5 times. Whilst, the inner crucible should be replaced at every measurement.

III. Results and Discussion

1. Lowering of blank values

The sources of oxygen blank in the LECO TC-436 apparatus are considered to be carrier gas, graphite crucible and adsorbed gases on the inner wall of the apparatus. Attaching importance to these three sources, the following experiments were conducted in order to examine the lowering of oxygen blank. Prior to each experiment, the oxygen blank in the apparatus was stabilized by passing a carrier gas at a flow rate of 450 cm³/60 s for more than 86.4 ks.

(1) Purification of He gas

Original gas refining system of the LECO TC-436 apparatus consists of granular Cu which takes up O₂, granular NaOH which captures acidic gases, and Mg(ClO₄)₂ which absorbs H₂O. However, the degree of purification attained with the original system, particularly that of the removal of water, is not satisfactory. Moreover, a period in which the system is active is short

because of the small amounts of the packed reagents. Repack of the reagents allow the invasion of air into the carrier gas tubing.

In this study, we used a "Dry Column" and a "Gas Clean" column as mentioned in II.1. These columns were usable for more than twelve months without repack of refining reagents. Lowering of oxygen blank by the new system was satisfactory in order to determine trace oxygen in high purity iron, although it was difficult to evaluate the merit of the system quantitatively.

(2) Oxygen blank value of double graphite crucible

In general, the oxygen blank in a double graphite crucible increases with gas extraction time. In the analysis of the sample containing a large amount of oxygen, the influence is negligible because a short gas extraction time of 20 s to 40 s is usually selected. Moreover, even if the gas extraction is incomplete, it does not largely influence the determination because of a sufficient amount of the oxygen to be extracted. However, in the analysis of the sample containing only a trace of oxygen, the complete gas extraction is indispensable. Thus, a gas extraction time of 100 s was selected for a series of the experiments described below.

Figure 3 shows the effect of repeated degassing of a double graphite crucible on the oxygen blank values in it. The degassing was repeated 4 times, where the degassing time of the outer crucible was 120 s for each run, and the inner crucible was replaced with a new one every run. After the temperature of the double crucible had dropped to the analytical temperature, oxygen blank values were measured over the gas extraction time of 50 s to 100 s by a 10 s step. As shown in Fig. 3, the oxygen blank values decreased significantly with the repetition of

Fig. 3 Oxygen blank values in the double graphite crucible by the conventional method.

degassing of the outer crucible, and the values became almost constant after 3 times repetition. However, the blank values were still too high to determine trace oxygen in high purity iron. The value for the extraction time of 100 s was about 0.5 mass ppm O. Further lowering of the blank value is probably difficult because the temperature rise at the bottom of the crucible is not sufficient owing to the direct cooling due to a water-cooled electrode.

(3) Deoxidation of outer crucible with molten silicon

Kashima *et al.*⁽⁴⁾ studied the deoxidation of a graphite crucible with molten Si at about 2273 K and obtained the following conclusion; the molten Si penetrated into the wall of the graphite crucible and formed SiC, which reacted with ash component of the graphite crucible. Nishi *et al.*⁽⁶⁾ examined vacuum degassing of a graphite crucible in the determination of trace oxygen in pure copper samples. Although vacuum degassing was considered as an effective procedure to lower the oxygen blank, we examined silicon deoxidation for an outer graphite crucible.

A semiconductor grade silicon (99.9999%) with an oxygen content below 10 ppm was used. An outer graphite crucible containing a given amount of the Si of 5 to 30 mg was heated for 100 s with a power of 4.5 ± 0.2 kW; the temperature was about 2373 K at the inner bottom face of the outer crucible. The crucible was then degassed for 60 s and the oxygen blank value for a period of 100 s was measured. Figure 4 shows the effect of the amount of Si on the oxygen blank in the outer crucible. Each blank value is the average of five measurements. By the addition of Si of 20 mg or more, the oxygen blank became undetectable. Moreover, it was found that at least 60 s was required to deoxidize the crucible. Basing upon these results, the addition of 25 mg of Si and a deoxidation time of 80 s was selected.

In the deoxidation of a graphite crucible with Si by high frequency heating, molten Si penetrates the whole of the crucible from the bottom to the upper portion⁽¹⁰⁾⁽¹¹⁾. However, the behavior of molten silicon in an impulse-heated graphite crucible has not yet been studied. Hence, the cross-section of an outer graphite crucible was observed after deoxidation under the conditions mentioned above. Figure 5 shows an illustration of the cross section of the vertically cut crucible. A penetration layer (0.5–1.5 mm deep) and a deposition band (2 mm wide) of Si were found respectively inside the bottom face and on the inner-wall near the mouth of the crucible. Both the substance of the layer and that of the band were confirmed to be SiC by means of EPMA. Such a SiC deposition was not found on the wall of the intermediate part; this is probably due to a higher temperature (above about 2673 K) of the part. A portion of the added Si deposited outside the crucible. Hence, a temperature below 2373 K is preferable. The significant lowering of oxygen blank by this method is due to the penetration of Si into the crucible bottom where degassing by the conventional heating method is difficult.

Fig. 4 Effect of the amount of Si on the decrease of oxygen blank values in the outer crucible.

Fig. 5 Outer crucible treated by heating at about 2373 K for 80 s with 25 mg of Si.

(4) Degassing of inner crucible

As for the degassing of an inner crucible, degassing only by heating is considered satisfactory, because the inner crucible is heated throughout with an impulse-heated outer crucible. Furthermore, the bottom of the inner crucible locates in the higher temperature part of the outer crucible. Examined was a relation between degassing time of an inner crucible and oxygen blank values in it. The outer crucible used was a deoxidized and degassed one, and the inner crucible was changed for a new one every measurement. Figure 6 shows the result in which each experimental point denotes the average of five measurements. The oxygen blank value decreased with an increase of the degassing time and became to below 0.01 mass ppm O/100 s in a degassing time of 120 s.

In the conventional procedure of the inert gas fusion method, gas extraction temperature (analytical temperature) is generally selected to a temperature about 200 K lower than that of degassing. Effect of the difference between both temperatures on the oxygen blank values was studied. After a degassing temperature of 2573 K had been preset, gas extraction temperature was changed from 2373 K to 2573 K at a step of 100 K, and the blank values at the temperatures were measured. Smaller the

Fig. 6 Effect of degassing time on the decrease of oxygen blank values in the inner crucible.

temperature difference, a higher blank value was obtained, and it was confirmed that a difference greater than 200 K was necessary.

Furuya *et al.*⁽¹²⁾, who studied the determination of trace oxygen in high purity iron by a vacuum fusion method, reported that a Sn bath was effective to minimize the oxygen loss which was caused by the chemisorption of the evolved gas onto the evaporated metal films. Hence, relating to the gas extraction using a Sn bath, the lowering of the oxygen blank in a double graphite crucible was examined. One gramme of Sn (LECO No. 761-739) was used as a bath material. A comparison was made between the following two cases: (a) 120 s continuous degassing with Sn, (b) 60 s degassing without Sn and subsequent 60 s degassing with Sn. The blank values lowered similarly for both case (a) and case (b). However, the use of more than 1 g of Sn made the degassing of itself imperfect and that of below 0.5 g did not left a sufficient amount of Sn after the degassing. Moreover, it was found that the contamination of the crucible with the vapor of Sn proceeded with the length of degassing time. Thus, the analytical operation using 0.75 g of Sn were decided as mentioned in II.5.

(5) Influence of the adsorbed gas in the apparatus

By admitting a carrier gas flow to the LECO TC-436 determinator, the oxygen blank in the apparatus lowered gradually. As a cause of the lowering, it is reasonable to consider the decrease of adsorbed gases in the carrier gas tubing (stainless steel tubes: 3.18 mm in I.D. and 3 m in total length). The tubing consisted of a gas tube (a) between the gas refining system and the impulse furnace and that (b) between the furnace and the IR detector (see Fig. 1). Heating of the tube (a) lowered rapidly the oxygen blank in a double graphite crucible, whilst the tube (b)

did not show the effect due to heating. From these results, it is clear that the adsorbed water in the gas tube (a) was released by heating, transferred into the furnace and changed to CO gas which gave oxygen blank.

The effect of heating of the gas tube (a) was further examined. A greater part (about 2 m) of the gas tube was heated at 403 K with a carrier gas flow of 450 cm³/60 s and then cooled to room temperature. After the admittance of the gas flow had been ceased, the furnace was opened by lifting its shell, and the furnace-side end of the gas tube was released. This induced the invasion of air into the tube; the humidity of the air was about 50%. After 129.6 ks later, the furnace was closed again and the oxygen blank values were measured every 1.8 ks by passing the carrier gas at a flow rate of 450 cm³/60 s. Figure 7 shows a comparison of the oxygen blank values for the cases with and without the heating of the tube (a). In the case with the heating, blank values decreased rapidly with the length of purge time of the carrier gas and reached 0.01 mass ppm O/150s in 7.2 ks. While, the decrease of blank value in the case without the heating was slower than that in the case with heating and became much slower in a period after 10.8 ks. Furthermore, even in the case with heating, the observed values of oxygen blank were affected by the humidity of the air. This is probably due to the adsorbed water on the wall of the un-heated part (about 1 m) which was difficult of tube-heating.

Further lowering of the oxygen blank can probably be attained either by replacing the gas tube (a) with a mirror-surface finished stainless steel tube on which gas adsorption is difficult, or by attaching a stop-cock which prevents the invasion of air into the gas tube.

Fig. 7 Oxygen blank values influenced by the water adsorbed on the inner-wall of the carrier gas tube.

(6) Graphite materials of the crucibles

Crucible blank is known to be affected also by the properties of the graphite materials. In the experiments using a vacuum fusion method, it has been reported that the blank values were influenced by the porosity rather than the purity of the crucible used⁽¹³⁾. Thus, two kinds of graphite crucibles with different properties were compared; one is a porous graphite crucible (a) and the other is an equiaxed high density graphite crucible (b). The former contained 40 ppm of ash and the latter 20 ppm of ash. Five crucibles were selected from each crucible group by random sampling. After 120 s degassing, blank values were measured by a step of 10 s with in a range from 50 s to 100 s, and the averages were plotted against gas extraction time. As shown in Fig. 8, the smaller ash-content crucible offered lower blank values than the larger ash-content one. Though the predominance of the porous crucible was not confirmed, this is probably related to a short degassing time comparing with the case of the vacuum fusion method.

Heating rates were almost the same for the two kinds of the crucibles used.

2. Application to the practical samples

(1) Gas extraction

Two kinds of high purity irons⁽¹⁾ provided from Tohoku University were analyzed; the oxygen content of sample A was smaller than that of sample B. Figure 9 shows the gas extraction curves which were obtained using the analytical specimens prepared according to the proposed procedure (II.5). The gas extraction of the lower oxygen content sample A started later than that of the sample B and depicted a gentle extraction curve with a long tail. In the conventional analysis, the final state of

Fig. 8 Comparison of oxygen blank values in double graphite crucibles with different porosities and ash-contents; (a) porous graphite crucible with the ash content of ca. 40 ppm, (b) high density graphite crucible with the ash content of ca. 20 ppm.

Fig. 9 Gas extraction curves of the samples containing different amounts of trace oxygen.

gas extraction in such a case was not obvious owing to a high oxygen blank. However, the gas extraction curves in Fig. 9 showed the completion of gas extraction clearly: the sample A, 90 s; the sample B, 100 s. Thus, it is found that a gas extraction time more than 90 s is necessary for the precise determination of trace oxygen in those samples.

(2) Effect of Sn addition

Table 1 shows the effects of a Sn bath in the gas extraction of the samples A and B. Analytical specimens were electro-polished by the method (b) and 0.75 g of Sn was added for 1 g of each sample. The addition of Sn made the gas extraction more complete, giving higher oxygen values with smaller RSD values. Lower oxygen values in the case without Sn addition are probably related to either the CO getter action of iron deposits on the crucible-wall or the lower fluidity of the molten iron sample. However, the getter action in an inert gas fusion method is not so strong as that in a vacuum fusion method. Therefore it seems reasonable to consider that the addition of Sn hinders the dissolution of carbon from the crucible-wall and consequently the increased fluidity promotes the gas extraction from the sample. A suitable amount of Sn was from 0.5 g to 1.0 g.

(3) Pretreatment procedures

As for the pretreatment of analytical specimens, various procedures have been investigated relating to the

Table 1 Effect of addition of Sn.

Sample	Sn mass (g)	Analyzed value (mass ppm)						$\bar{x}$ (mass ppm)	RSD (%)
A	0	1.5	1.2	1.5	0.9	1.2		1.26	19.9
	0.75	1.4	1.4	1.4	1.5	1.6		1.46	6.1
B	0	4.7	4.8	4.9	4.5	5.1		4.80	4.7
	0.75	5.3	5.0	5.2	4.9	5.0		5.08	3.2

Samples treatment: electrolytic polishing method (b).

Table 2 Comparison of analytical oxygen values for high purity iron samples treated with different methods.

Sample	Method	Analyzed* value (mass ppm)	Analyzed value (mass ppm)					$\bar{x}$ (mass ppm)	RSD (%)
A	(a)	1.2±0.04	1.6	1.6	1.4	1.6	1.7	1.58	6.9
	(b)		1.6	1.6	1.5	1.6	1.4	1.54	5.8
	(c)		1.6	1.7	1.6	1.6	1.7	1.64	3.3
	(d)		1.1	1.3	1.1	1.3	1.2	1.20	8.3
B	(a)	4.8±0.1	5.2	4.9	5.0	4.9	5.2	5.04	3.0
	(b)		5.0	5.0	5.2	4.9	5.0	5.02	2.2
	(c)		5.0	5.1	5.3	5.2	5.1	5.14	2.2
	(d)		4.8	4.9	4.8	4.8	4.9	4.84	1.1

* Charged particle activation analysis method.

determination of trace oxygen⁽⁶⁾⁽⁹⁾⁽¹⁰⁾⁽¹²⁾⁽¹⁴⁾. It is known for high purity iron that the amount of oxygen remaining on the surface of an analytical specimen depends on the pretreatment procedure of the specimen⁽¹²⁾. In this study, four kinds of the procedures described in II.3. (a)–(d) were examined for the high purity iron samples A and B. Table 2 shows a comparison of the oxygen values obtained for the specimens treated with different methods and the values determined by the charged particle activation analysis⁽¹⁵⁾. The activation analysis is capable of determining the concentration of oxygen in the bulk, irrespective of the presence of surface oxide films.

As for the analytical values of the sample A, significant difference among the chemical polishing (a), the electro-polishing (b) and electro-polishing (c) was not found. However, hydrogen reduction by Ar–5% H₂ (d) following the electro-polishing (c) offered lower oxygen values. A similar tendency was also found for the analytical results of the sample B. Since the analytical values of the specimens which were treated with Ar–5% H₂ agreed well with the results of the activation analysis, it was suggested that the specimens pretreated by the methods (a)–(c) suffered oxidation with air. Moreover, the influence of surface oxidation was found to be larger for the sample with a lower oxygen content.

IV. Conclusion

Determination of trace oxygen in high purity iron was investigated for the inert gas fusion-infrared absorption method using an impulse heating technique.

(1) Helium carrier gas (99.999% pure) was further purified with commercial gas-refining columns: “dry column” for the removal of trace water; “gas clean” column for the removal of trace oxygen. These columns were usable for a long period of twelve months and more without exchange.

(2) Oxygen blank in an outer crucible was significantly reduced by heating the crucible at 2373 K for 80 s with Si above 20 mg. Oxygen blank in a double crucible was reduced to below 0.01 mass ppm O/100 s by degassing

an inner crucible at 2573 K for 120 s with the outer crucible which had been deoxidized with Si.

(3) The source of the oxygen blank in the apparatus was found to be the trace water adsorbed on the inner-wall of a carrier gas tube. With the removal of the adsorbed water, the oxygen blank in a double graphite crucible also stabilized and decreased to below 0.01 mass ppm O/150 s.

(4) A lower ash-content crucible gave a more correct analytical value than a crucible with a higher ash content, although the influence of their porosities was not clearly found.

(5) A gas-extraction time more than 90 s was necessary for the precise determination of ppm-level oxygen.

(6) The use of a Sn bath was indispensable to evolve gases from the analytical sample completely.

(7) As-pretreated analytical specimens with chemical-polishing or electro-polishing suffered oxidation in the air. Hydrogen reduction following electro-polishing was found to be suitable to determine oxygen of below 5 mass ppm. The RSD-values were 8.3% for 1.2 mass ppm O and 1.1% for 4.8 mass ppm O. These determined values agreed very closely with the results of charged-particle activation analysis.

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